

1 **PROCESS FOR MAKING GROUP II METAL CARBONATED,**
2 **OVERBASED MANNICH CONDENSATION PRODUCTS**
3 **OF ALKYLPHENOLS**

4 FIELD OF THE INVENTION

5 This invention is directed to a novel process for making Group II metal
6 carbonated, overbased Mannich condensation products of alkylphenols,
7 which process uses ethylene carbonate as both a source of carbon dioxide
8 and ethylene glycol. In particular, under the reaction conditions using
9 ethylene carbonate in the present invention, overbasing of Mannich
10 condensation products of alkylphenols is possible while at the same time
11 viscosity of the carbonated, overbased Mannich condensation products of
12 alkylphenols remains within acceptable levels, typically under 1000 cSt at
13 100°C. This invention is also directed to a process for making Group II metal
14 carbonated, overbased Mannich condensation products of alkylphenols,
15 which process uses carbon dioxide and ethylene glycol. The present
16 invention is also directed to a detergent-dispersant antioxidant additive
17 composition comprising Group II metal carbonated, overbased Mannich
18 condensation products of alkylphenols, wherein the Group II metal
19 carbonated, overbased Mannich condensation products of alkylphenols have
20 a CO₂ to Ca ratio of at least 0.01.

21 The present invention is also directed to a lubricating oil additive comprising
22 Group II metal carbonated, overbased Mannich condensation products of
23 alkylphenols, which is low in sulfur content, typically less than 0.3 percent as
24 measured by ASTM Test No. D 4951-92.

25 The present invention is also directed to a Mannich condensation product
26 comprising a reaction product of an alkylphenol, an aldehyde and
27 N-phenyl-1,4-phenylene diamine.

1

BACKGROUND OF THE INVENTION

2 The operation of diesel and spark ignition internal combustion engines is
3 typically accompanied by the formation of sludge, lacquer and resinous
4 deposits which adhere to the moving engine parts and thereby reduce engine
5 efficiency. In order to prevent or reduce the formation of these deposits, a
6 wide variety of chemical additives have been developed for incorporation into
7 lubricating oils. These additives are commonly referred to as detergents and
8 dispersants. Dispersants have the ability to keep deposit forming materials
9 suspended in the oil so as to retard deposit formation during engine operation.
10 Detergents have the ability to remove pre-existing deposits from the engine
11 during engine operation and to neutralize acids in railroad, marine and
12 automotive engines.

13 A large number of railroad and tugboat diesel engines use silver-plated
14 bearings. As a result, the lubricating oil requires acceptable silver wear
15 control and corrosion performance in addition to deposit control and alkalinity.
16 Mannich bases and their salts have been known to be effective to protect
17 silver bearing parts in such engines without the disadvantages associated
18 with the use of chlorinated and dithiophosphate additives.

19 Mannich bases and their salts are also known to be particularly useful in
20 lubricating oils, fuels, greases and plastics as antioxidants. Hydrocarbon
21 materials are highly susceptible to chemical action on aging, exposure to
22 sunlight and in their normal use. Such oxidation can lead to the deposit of
23 undesirable residues in lubricants, fuels and greases and to discoloration of
24 plastics.

25 Frequently, the inclusion of additives in lubricating oils and fuels to control
26 deposits, wear and oxidation cause compatibility problems. In addition, it is
27 uneconomical to add many additives in order to achieve all these functions.

1 Thus, there is a great need for the development of a single multifunctional
2 agent that will perform all these desired functions.

3 One class of lubricating oil additives typically used as dispersants, detergents,
4 oxidation inhibitors and anti-wear additives are Mannich condensation
5 products of an alkylphenol, an aldehyde and an amine.

6 Various Mannich condensation products known in the prior art as lubricating
7 oil additives are metal salts. Currently, there is no carbonation process in the
8 prior art for making Group II metal carbonated, overbased Mannich
9 condensation products of alkylphenol which have a high alkalinity reserve for
10 neutralizing acids in engines and at the same time have acceptable viscosity.
11 It is believed that the carbonate, overbased Mannich condensation products
12 of alkylphenols of the present invention are superior to the prior art salts of
13 Mannich condensation products of alkylphenols for providing the functions of
14 detergent-dispersants, anti-wear and oxidation agents in one additive
15 because of their greater alkalinity reserve and acceptable viscosities.

16 The ability of additive compositions to neutralize acids in engines can be
17 measured by determining the total base number (TBN) or the alkalinity
18 reserve of the composition. Higher TBNs reflect a greater capacity for these
19 compositions to neutralize acids generated during engine operation.
20 However, the TBN of a composition is directly related to the amount of diluent
21 oil present. Thus, more concentrated compositions will have a higher TBN
22 than those containing more diluent.

23 The preparation of Group II metal salts of Mannich condensation products of
24 alkylphenol compositions is well known in the art. A number of patents have
25 discussed processes for making Group II metal salts of the Mannich
26 condensation products of alkylphenols, but none have included a carbonation
27 step in the process.

1 For example, U.S. Pat. No. 3,036,003 discloses a process for making a metal
2 salt of a condensation product of an alkylene polyamine, an aldehyde and
3 substituted phenol.

4 U.S. Pat No. 3,340,190 discloses the preparation of a mixture of the exactly
5 neutralized calcium salt of N,N'-bis(alkyl substituted hydroxybenzyl) alkylene
6 diamine and a bis (alkenylsuccinimide) of polyalkylene polyamine or of a urea
7 condensation derivative of polyalkylene polyamine,
8 N,N'-bis(polyazalkylamino) ureylene.

9 U.S. Pat. No. 3,586,629 discloses the preparation of salts obtained by
10 reacting the condensation product of an alkyl hydroxy aromatic compound, an
11 aldehyde and an amine or alkali metal salt thereof with a metal base. These
12 salts provide excellent detergency characteristics to an organic industrial fluid.

13 U.S. Pat. No. 3,798,163 teaches a method for inhibiting exhaust valve
14 recession in natural gas fueled internal combustion engines with the use of
15 composition comprising a lubricating oil, a metal sulfonate and at least one
16 metal salt of a condensation product of an alkylene polyamine, an aldehyde
17 and a substituted phenol.

18 U.S. Pat. No. 3,958,624 discloses an improved anti-fouling additive for use in
19 organic heat transfer fluids comprising a combination of a barium overbased
20 calcium sulfonate and a phenolic antioxidant, an alkaline earth aminophenate.

21 U.S. Pat. No. 4,025,316 discloses the preparation of polymeric alkyl-hydroxy
22 benzyl N-substituted amines having a high degree of ring formation derived
23 from the condensation reaction of C₈-C₄₀ aliphatic alkyl substituted hydroxy
24 aromatic, an aldehyde and an amine.

25 U.S. Pat. No. 4,088,586 discloses the preparation of salts of Mannich bases
26 from tetrapropenylphenol, formaldehyde and diethylenetriamine when the

1 molar ratio of the reactant is 1 mole tertapropenylphenol to 0.5 to 0.85 mole
2 formaldehyde to at least 0.3 mole of diethylenetriamine having outstanding
3 viscosity and alkalinity value properties.

4 U.S. Pat. No. 4,140,492 discloses the preparation of borated derivatives of
5 oil-soluble Mannich bases for use in combination with coadditive
6 hydrocarbons for flow improvers for middle distillate fuel oils.

7 U.S. Pat. Nos.4,157,308 discloses the preparation of Mannich base
8 compositions and their metal salts from phenolic mixtures consisting of phenol
9 alkylated with a propylene tetramer and phenol alkylated with a straight-chain
10 alpha-olefin.

11 U.S. Pat. No. 4,231,759 discloses a liquid hydrocarbon combustion fuel
12 containing an additive composition comprising the Mannich condensation
13 product of a high molecular weight alkyl-substituted hydroxyaromatic
14 compound wherein the alkyl group has a molecular weight of from about 600
15 to about 3,000.

16 U.S. Pat. No. 4,655,949 discloses novel lubricating oil composition comprising
17 an organometallic additive containing a metal selected from Groups I, Ib and
18 VIII chelated with the reaction product of formaldehyde, an amino acid and a
19 phenol.

20 U.S. Pat. Nos. 4,734,211; 4,764,296 and 4,820,432 disclose a lubricating oil
21 composition for railway diesel engines which contains calcium salt of Mannich
22 reaction product among other additives. The Mannich base is prepared using
23 an alkyl substituted hydroxy aromatic compound, specifically para-alkyl
24 phenol. The TBN of the product was approximately 160.

25 Typically, Mannich bases are prepared by reacting an alkylphenol with an
26 aldehyde and an amine wherein the amine is a primary or secondary aliphatic

1 or aromatic amine or polyamine, and the aldehyde is an aliphatic or aromatic
2 aldehyde. The alkyl group of the phenol can be straight-chain or branched-
3 chain. Optionally, a promoter may be used during the condensation reaction.

4 The prior art process for making the metal salt of the Mannich bases is
5 typically by the addition of a metal oxide, hydroxide or hydroperoxide.
6 Optionally, ethylene glycol is added to the reaction mixture to promote the salt
7 formation.

8 SUMMARY OF THE INVENTION

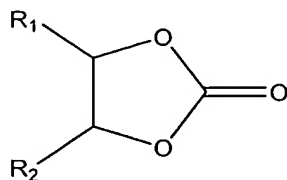
9 The present invention is directed to a novel process for making Group II metal
10 carbonated, overbased Mannich condensation products of alkylphenols,
11 which process uses ethylene carbonate as both a source of carbon dioxide
12 and ethylene glycol. In particular, under the reaction conditions using
13 ethylene carbonate in the present invention, overbasing, as defined herein, of
14 Mannich alkylphenols is possible while at the same time the viscosity of the
15 carbonated, overbased Mannich condensation products of alkylphenols
16 remains within acceptable levels, typically under 1000 cSt at 100°C. This
17 invention is also directed to a process for making Group II metal carbonated,
18 overbased Mannich condensation products of alkylphenols, which process
19 uses carbon dioxide and ethylene glycol. The present invention is also
20 directed to a detergent-dispersant antioxidant additive composition comprising
21 Group II metal carbonated, overbased Mannich condensation products of
22 alkylphenols, wherein the Group II metal carbonated, overbased Mannich
23 condensation products of alkylphenols have a CO₂ to Ca ratio of at least 0.01.

24 The present invention is also directed to a lubricating oil additive comprising
25 Group II metal carbonated, overbased Mannich condensation products of
26 alkylphenols, which is low in sulfur content, typically less than 0.3 percent as
27 measured by ASTM Test No. D 4951-92. It is believed that the sulfur content
28 in the Group II metal carbonated, overbased Mannich condensation products

1 of alkylphenols of the present invention is contributed by the diluent used in
2 the preparation of the Group II metal carbonated, overbased Mannich
3 condensation products of alkylphenols.

4 In particular, the process of the present invention for preparing Group II metal
5 carbonated, overbased Mannich condensation products of alkylphenols
6 comprises:

7 forming a reaction mixture by combining a Mannich condensation product of
8 an alkylphenol wherein the alkyl group contains a sufficient number of carbon
9 atoms to render oil-soluble the resulting Group II metal carbonated,
10 overbased Mannich condensation product of alkylphenol, a Group II metal
11 oxide, hydroxide or C₁-C₆ alkoxide, in the presence of a promoter and
12 optionally a second promoter, and an alkylene carbonate selected from
13 ethylene carbonate or a mono-alkyl or di-alkyl substituted ethylene carbonate,
14 said alkylene carbonate having the following structure:



15
16 wherein R₁ and R₂ are independently hydrogen or alkyl containing one to
17 three carbon atoms; and wherein the combining is carried out for a time and
18 at a temperature sufficient to form in situ carbon dioxide and alkylene glycol,
19 or a reacting equivalent, to form a product comprising a Group II metal
20 carbonated, overbased Mannich condensation product of alkylphenol.

21 In the alkylene carbonate structure above, preferably one of R₁ and R₂ is
22 hydrogen and the other is hydrogen or methyl. In other words, the alkylene
23 carbonate is preferably ethylene carbonate or propylene carbonate. More
24 preferably, R₁ and R₂ are both hydrogen; that is, the alkylene carbonate is
25 ethylene carbonate.

1 In another embodiment, the Mannich condensation product of alkylphenol
2 used in the process of the present invention as described above may be
3 replaced with a Group II metal salt.

4 A further embodiment of the present invention is directed to a process for
5 making Group II metal carbonated, overbased Mannich condensation
6 products of alkylphenols, in which process a C₂-C₁₀ alkylene glycol and
7 carbon dioxide replace the alkylene carbonate. Preferably, the C₂-C₁₀
8 alkylene glycol is ethylene glycol.

9 The alkylene carbonate is added to the reaction mixture over a time period of
10 about 15 minutes to about 120 minutes. Preferably, the alkylene carbonate is
11 added to the reaction mixture over a time period of about 30 minutes to about
12 90 minutes, and more preferably the alkylene carbonate is added to the
13 reaction mixture over a time period of about 40 minutes to about 60 minutes.

14 The promoter used in the process of the present invention is typically a C₂-C₁₀
15 alkylene glycol.

16 The promoter optionally used in the process of the present invention may
17 typically include water, a C₁-C₅ mono- or di-alcohol or a C₂-C₁₀ alkylene glycol
18 or a mixture thereof. Preferably, the promoter optionally used is a C₂-C₁₀
19 alkylene glycol, and more preferably the promoter optionally used is water.

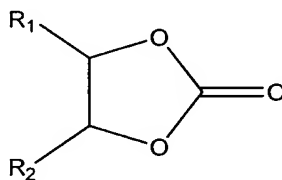
20 Optionally, the process of the present invention further comprises the step of
21 recovering the product by filtering the reaction mixture to remove sediment.

22 An alternate embodiment of the present process for preparing Group II metal
23 carbonated, overbased Mannich condensation products of alkylphenols
24 comprises the steps of:

25 (a) forming a reaction mixture by combining a Mannich condensation
26 product of alkylphenol wherein the alkyl group contains a sufficient

number of carbon atoms to render oil-soluble the resulting Group II metal carbonated, overbased Mannich condensation product of alkylphenol, a Group II metal oxide, hydroxide or C₁-C₆ alkoxide, a promoter and optionally a second promoter; and

(b) contacting said reaction mixture with an alkylene carbonate selected from ethylene carbonate or a mono-alkyl or di-alkyl substituted ethylene carbonate, said alkylene carbonate having the following structure:



wherein R₁ and R₂ are independently hydrogen or alkyl containing one to three carbon atoms; and wherein the contacting is carried out for a time and at a temperature sufficient to form in situ carbon dioxide and alkylene glycol, or a reacting equivalent, to form a product comprising a Group II metal carbonated, overbased Mannich condensation product of alkylphenol.

In the alkylene carbonate structure above, preferably one of R₁ and R₂ is hydrogen and the other is hydrogen or methyl. In other words, the alkylene carbonate is preferably ethylene carbonate or propylene carbonate. More preferably, R₁ and R₂ are both hydrogen; that is, the alkylene carbonate is ethylene carbonate.

The Mannich condensation product of alkylphenol used in the alternate embodiment of the process of the present invention as described above may be replaced with a Group II metal salt.

1 A further embodiment of the alternate embodiment is directed to a process for
2 making Group II metal carbonated, overbased Mannich condensation
3 products of alkylphenols, in which process a C₂-C₁₀ alkylene glycol and
4 carbon dioxide replace the alkylene carbonate in step (b). Preferably, the
5 C₂-C₁₀ alkylene glycol is ethylene glycol.

6 The alkylene carbonate is added to the reaction mixture over a time period of
7 about 15 minutes to about 120 minutes. Preferably, the alkylene carbonate is
8 added to the reaction mixture over a time period of about 30 minutes to about
9 90 minutes, and more preferably the alkylene carbonate is added to the
10 reaction mixture over a time period of about 40 minutes to about 60 minutes.

11 The promoter used in step (a) of the above process of the present invention is
12 a C₂-C₁₀ alkylene glycol.

13 The promoter optionally used in step (a) of the process is typically water, a
14 C₁-C₅ mono- or di-alcohol or a C₂-C₁₀ alkylene glycol or a mixture thereof.
15 Preferably, the promoter optionally used is a C₂-C₁₀ alkylene glycol, and more
16 preferably the promoter optionally used is water.

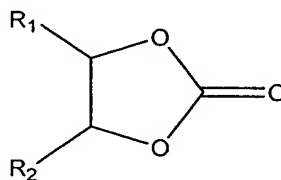
17 Optionally, the process of this embodiment further comprises the step of
18 recovering the product by filtering the reaction mixture to remove sediment.

19 Another embodiment of the present process for preparing Group II metal
20 carbonated, overbased Mannich condensation products of alkylphenols
21 comprises the steps of:

22 (a) forming a first reaction mixture by combining an alkylphenol
23 wherein the alkyl group contains a sufficient number of carbon
24 atoms to render oil-soluble the resulting Group II metal carbonated,
25 overbased Mannich condensation product of alkylphenol, an
26 aldehyde and an amine and a promoter optionally used;

1 (b) contacting said first reaction mixture with a second reaction mixture
2 comprising a Group II metal oxide, hydroxide or C₁-C₆ alkoxide; an
3 inert hydrocarbon diluent, a promoter and optionally a second
4 promoter to form a third reaction mixture; and

5 (c) contacting said third reaction mixture with an alkylene carbonate
6 selected from ethylene carbonate or a mono-alkyl or di-alkyl
7 substituted ethylene carbonate, said alkylene carbonate having the
8 following structure:



9
10 wherein R₁ and R₂ are independently hydrogen or alkyl containing
11 one to three carbon atoms; and wherein said contacting is carried
12 out for a time and at a temperature sufficient to form in situ carbon
13 dioxide and alkylene glycol, or a reacting equivalent, to form a
14 product comprising a Group II metal carbonated, overbased
15 Mannich condensation product of alkylphenol.

16 In the alkylene carbonate structure above, preferably one of R₁ and R₂ is
17 hydrogen and the other is hydrogen or methyl. In other words, the alkylene
18 carbonate is preferably ethylene carbonate or propylene carbonate. More
19 preferably, R₁ and R₂ are both hydrogen; that is, the alkylene carbonate is
20 ethylene carbonate.

21 In step (a) of the above embodiment of the present invention, the temperature
22 of reaction mixture is in the range of about 35°C to about 170°C.

23 A further embodiment is directed to a process for making Group II metal
24 carbonated, overbased Mannich condensation products of alkylphenols, in

1 which process a C₂-C₁₀ alkylene glycol and carbon dioxide replace the
2 alkylene carbonate in step (c). Preferably, the C₂-C₁₀ alkylene glycol is
3 ethylene glycol.

4 The alkylene carbonate is added to the reaction mixture over a time period of
5 about 15 minutes to about 120 minutes. Preferably, the alkylene carbonate is
6 added to the reaction mixture over a time period of about 30 minutes to about
7 90 minutes, and more preferably the alkylene carbonate is added to the
8 reaction mixture over a time period of about 40 minutes to about 60 minutes.

9 The promoter used in step (b) of the process of the above present
10 embodiment is a C₂-C₁₀ alkylene glycol.

11 The promoter optionally used in step (b) of the above present embodiment is
12 typically water, a C₁-C₅ mono- or di-alcohol or a C₂-C₁₀ alkylene glycol or a
13 mixture thereof. Preferably, the promoter is a C₂-C₁₀ alkylene glycol, and
14 more preferably the promoter is water.

15 In step (a), the amine may be an aliphatic amine, an aromatic amine, a
16 polyfunctional amine, such as ethanol amine, or mixtures thereof, containing
17 at least one amino group characterized by the presence of at least one active
18 hydrogen or methylene group, and wherein the amine contains only primary
19 amino groups, only secondary amino groups, or both primary and secondary
20 amino groups.

21 The aliphatic amine may be an alkylene diamine, a dialkylamine, a
22 polyalkylene polyamine or mixtures thereof. The aromatic amine may be a
23 single-ring aromatic amine or a double-ring aromatic amine.

24 In step (a), the aldehyde may be an aliphatic aldehyde, aromatic aldehyde, a
25 heterocyclic aldehyde or mixtures thereof. Preferably, the aliphatic aldehyde

1 is formaldehyde or paraformaldehyde, the aromatic aldehyde is
2 benzaldehyde, and the heterocyclic aldehyde is furfural.

3 The molar ratios of the alkylphenol, the aldehyde and the amine in step (a)
4 are from about 1:1.8:1 to about 1:3:1.

5 The alkyl group of the alkylphenol may be straight-chain or branched-chain
6 and will typically contain at least 10 carbon atoms, preferably from about
7 12 carbon atoms to about 50 carbon atoms.

8 Preferably, the alkyl group of the alkylphenol contains from about 25 to about
9 100 mole percent predominantly straight-chain alkyl groups containing from
10 about 15 to about 35 carbon atoms and from about 75 to about 0 mole
11 percent branched-chain alkyl groups containing from about 9 to about
12 18 carbon atoms. Preferably, the alkyl group of the alkylphenol contains from
13 about 40 to about 70 mole percent predominantly straight-chain alkyl groups
14 containing from about 15 to about 35 carbon atoms and from about 60 to
15 about 30 mole percent branched-chain alkyl groups containing from about 9 to
16 about 18 carbon atoms.

17 In a preferred embodiment, the alkyl group of the alkylphenol is attached
18 predominantly at the para position of the phenol ring. Preferably, the
19 alkylphenol containing the para attachment of the alkyl group is from about
20 70 to about 95 weight percent of the total alkylphenol. More preferably, the
21 alkylphenol containing the para attachment of the alkyl group is from about
22 80 to about 95 weight percent of the total alkylphenol.

23 The Group II metal oxide, hydroxide or C₁-C₆ alkoxide is selected from the
24 group consisting of calcium, barium, and magnesium oxide, hydroxide or
25 C₁-C₆ alkoxide and mixtures thereof. Preferably, the Group II metal oxide,
26 hydroxide or C₁-C₆ alkoxide is calcium hydroxide.

1 Optionally, the process of this embodiment further comprises the step of
2 recovering the product by filtering the reaction mixture to remove sediment.

3 The carbonation processes of the instant invention are particularly useful for
4 preparing Group II metal carbonated, overbased Mannich condensation
5 products of alkylphenols possessing a CO₂ to Ca ratio of at least about 0.01,
6 and preferably in the range of about 0.1 to about 0.6, and more preferably in
7 the range of about 0.3 to about 0.5.

8 The processes of the present invention may be carried out in a batch or a
9 continuous process. It is believed that small changes in pressure will have
10 little effect on the carbonation process of the present invention.

11 The present invention is also directed to a detergent-dispersant and
12 antioxidant additive comprising Group II metal carbonated, overbased
13 Mannich condensation products of alkylphenols, said additive having a CO₂ to
14 Ca ratio of at least about 0.01, and preferably in the range of about 0.1 to
15 about 0.6, and more preferably in the range of about 0.3 to about 0.5.

16 The detergent-dispersant antioxidant additive of the present invention
17 comprises Group II metal carbonated, overbased Mannich condensation
18 product of alkylphenol wherein the Mannich alkylphenol is a condensation
19 product of an alkylphenol, an aldehyde and an aliphatic, an aromatic, a
20 polyfunctional amine or mixtures thereof, said additive having a CO₂ to Ca
21 ratio of at least about 0.01, and preferably in the range of about 0.1 to about
22 0.6, and more preferably in the range of about 0.3 to about 0.5.

23 The present invention is also directed to a Mannich condensation product
24 comprising a reaction product of an alkylphenol, an aldehyde and
25 N-phenyl-1,4-phenylene diamine wherein the alkyl group of the alkylphenol is
26 a straight-chain alkyl group or branched-chain alkyl group containing from
27 about 10 carbon atoms to about 50 carbon atoms. Preferably, the alkyl group

1 of the alkylphenol has about 12 carbon atoms to about 24 carbon atoms. The
2 aldehyde is an aliphatic aldehyde, aromatic aldehyde, a heterocyclic aldehyde
3 or mixtures thereof. Preferably, the aliphatic aldehyde is paraformaldehyde or
4 formaldehyde. More preferably, the alkyl group of the alkylphenol has about
5 12 carbon atoms, the aldehyde is paraformaldehyde, and the amine is
6 N-phenyl-1,4-phenylene diamine in the Mannich condensation product of this
7 invention.

8 DETAILED DESCRIPTION OF THE INVENTION

9 DEFINITIONS

10 As used herein, the following terms have the following meanings unless
11 expressly stated to the contrary:

12

13 The term "alkoxide" means a compound which can be formed as the reaction
14 product of an alcohol and a reactive metal.

15

16 The term "alkylene glycol" means an aliphatic diol having two hydroxy groups
17 on adjacent carbon atoms.

18

19 The term "alkylphenol" means a phenol group having one or more alkyl
20 substituents, at least one of which has a sufficient number of carbon atoms to
21 impart oil solubility to the phenol.

22

23 The term "carbonated, overbased Mannich condensation products of
24 alkylphenols" means the products obtained after carbonation and overbasing,
25 as described in the process of the present invention, of Mannich bases
26 prepared by reacting an alkylphenol with an aldehyde and an amine wherein
27 the amine is a primary or secondary aliphatic or aromatic amine or polyamine,
28 the aldehyde is an aliphatic or aromatic aldehyde.

29

1 Use of the term "ethylene carbonate" includes alkyl-substituted alkylene
2 carbonate, such as propylene carbonate and the like.
3

4 The term "overbased" as used herein describes those Group II metal
5 carbonated, overbased Mannich condensation products of alkylphenols in
6 which the ratio of carbon dioxide to calcium is at least 0.01 and may be as
7 high as 0.6.
8

9 The term "promoter" means a C₂-C₁₀ alkylene glycol capable of assisting in
10 the carbonation step of the process of the present invention.

11 The term "promoter optionally used" means any polar chemical, such as
12 water, a C₁-C₅ mono- or di-alcohol or ethylene glycol or a mixture thereof, that
13 is capable of assisting in the process of the present invention.
14

15 The term "one or more promoters" means a promoter or a promoter optionally
16 used as defined herein.
17

18 The term "reacting equivalent" means any material equivalent to ethylene
19 glycol and carbon dioxide, such as the carbonic acid half ester.
20

21 Sulfur content was measured by ASTM Test No. D 4951-92.

22 The term "Total Base Number" or "TBN" refers to the amount of base
23 equivalent to milligrams of KOH in one gram of sample. The TBN of a sample
24 can be determined by ASTM Test No. D 2896 or any other similar procedure.
25

26 Calcium content of the carbonated, overbased Group II metal Mannich
27 condensation products of alkylphenols was measured using the following
28 procedure:
29

1 Samples of 0.5 grams to 2.0 grams placed in 8 milliliter vials with plastic-lined
2 screw caps and diluted with a solution of ortho-xylene that contains 8%
3 mineral oil, 340D, and a 50 ppm Ag internal standard element. Analysis is
4 done using the Inductively Coupled Plasma in an Inductively Coupled Plasma
5 Optical Emission Spectrometer. Results are reported as parts per million
6 (w/w) or weight percent.

7

8 Carbon dioxide content of the carbonated, overbased Group II metal Mannich
9 condensation products of alkylphenols was measured using the following
10 procedure:

11

12 Approximately 100 mg of sample is weighed into a test tube and acidified with
13 p-toluene sulfonic acid to release CO₂. The liberated gases are swept
14 through several scrubbers to remove interfering species. The resultant gas
15 stream is bubbled into a solution that contains mono-ethanol amine (MEA)
16 and a pH sensitive indicator. The addition of CO₂ to the solution changes the
17 pH, which changes the color of the indicator. The color change is sensed by
18 a visible spectrophotometer, and a controlling coulometer generates hydroxyl
19 ion at an electrode in the solution to bring the pH back to its original value.
20 The titration charge is related back to the original amount of acid evolved
21 carbon in the sample by means of Coulomb's law. The result is given as
22 weight percent CO₂.

23

24 Kinematic viscosity of the carbonated, overbased Group II metal Mannich
25 condensation products of alkylphenols was measured using the following
26 modified ASTM Test No. D 445:

27

28 A portion (1-5 milliliters) of sample is loaded into a calibrated Zeitfuchs
29 cross-arm viscometer. The sample and viscometer are brought to thermal
30 equilibrium by immersion in a temperature-controlled bath. The sample level
31 is brought to a mark on the viscometer. The sample is induced to flow by
32 applying a small momentary pressure; after the flow has begun, the sample

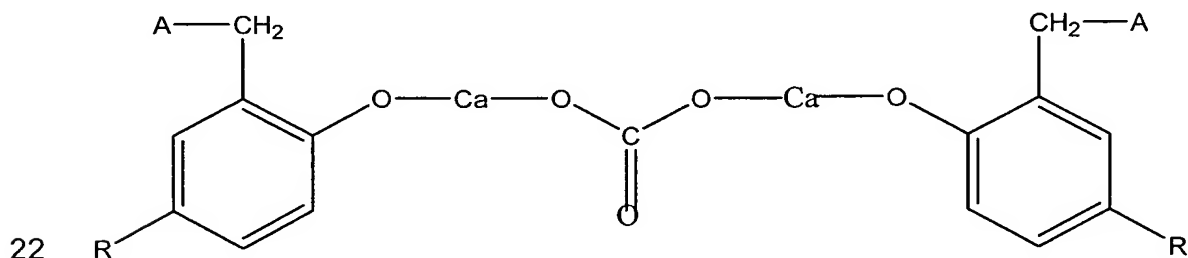
1 flows under gravity. The time is measured for the sample to flow between two
2 marks on the viscometer. The time is related to the sample viscosity by
3 means of the previously determined calibration constant. Results are
4 reported as centistokes at 100°C.

5 Unless otherwise specified, all percentages are in weight percent and the
6 pressure is atmospheric pressure.

7

8 It has been determined that the alkalinity reserve of the Group II metal
9 Mannich alkylphenols can be increased by the addition of a carbonation step
10 after the neutralization of the Group II metal Mannich condensation products
11 of alkylphenols with calcium hydroxide. The term "overbased" as used herein
12 describes those Group II metal Mannich condensation products of
13 alkylphenols in which the ratio of carbon dioxide to calcium is at least 0.01
14 and may be as high as 0.6. In contrast, the equivalent ratio of carbon dioxide
15 to calcium is 0.0 in uncarbonated Group II metal Mannich condensation
16 products of alkylphenol because the neutralization of Group II metal Mannich
17 condensation products of alkylphenol is generally carried out with calcium
18 hydroxide and without carbonation.

19 Without being bound by any theory, it is believed that one possible chemical
20 structure of the Group II metal carbonated-overbased product of the
21 carbonation step is as depicted below:



24 wherein R is alkyl and A is an amine or a polyamine.

1 Current automotive formulations require very low sulfur levels, less than
2 0.3 percent, and future formulations may require even lower levels of sulfur.
3 Thus, the additive itself must add little or no sulfur to the finished lubricating oil
4 product. However, conventional detergent-dispersant additives, such as
5 Group II metal overbased sulfurized alkylphenols, increase the sulfur content
6 of the finished lubricating oil product because of the high sulfur content of the
7 additive. The carbonated, overbased Mannich condensation products of
8 alkylphenol additives of the present invention have the distinct advantage over
9 the conventional detergent-dispersant additives in that the final sulfur content
10 of the additives is below 0.3 percent, which sulfur content may be present in
11 the diluent oil used for making the carbonated, overbased Mannich
12 condensation products of alkylphenols. The carbonated, overbased Mannich
13 condensation products of alkylphenols themselves do not contain sulfur.

14 As noted above, this invention is directed to a novel process for the rapid
15 carbonation of Mannich condensation products of alkylphenols using ethylene
16 carbonate or alkylene-substituted ethylene carbonate. We have discovered
17 that the ethylene carbonate in the carbonation step for the preparation of
18 carbonated, overbased Mannich condensation products of alkylphenols can
19 be used as both a source of carbon dioxide and ethylene glycol. Under the
20 reaction conditions using ethylene carbonate, rapid carbonation of Mannich
21 condensation products of alkylphenols is feasible for the preparation of
22 carbonated, overbased Mannich condensation products of alkylphenols which
23 has not been possible in the prior art processes.

24

25 The carbonation of Mannich condensation products of alkylphenols using the
26 processes of the present invention provide a product with good alkalinity
27 reserve and acceptable viscosity compared to the prior art salts of Mannich
28 condensation products of alkylphenols without any loss in the quality of the
29 product. The chemical and physical properties of the product of the present
30 process are also good, including high base content, low crude product
31 sediment and fast filtration rates.

EXAMPLES

General Procedure for Examples

Preparation of Carbonated, Overbased Mannich Condensation Products of Alkylphenols

Below is described the procedure generally used for the preparation of carbonated, overbased Mannich condensation products of alkylphenols in accordance with the present invention. Specific amounts used in the preparation of Examples 1-46 and A-E are given in Tables I and VI.

Into a 4 liter, 5-neck resin kettle reactor equipped with metal baffle insert, a turbine blade mechanical stirrer and a reflux condenser (closed at the top), the following components were combined:

- 804.8 grams of C₁₀-C₁₅ alkylphenol
- 7.5 grams of defoamer, polydimethylsiloxane, Dow Corning 200® purchased from Dow Corning
- 168.2 grams of paraformaldehyde
- 480.8 grams of 150 Neutral oil purchased from ExxonMobil, which contained 0.278 and 0.374 percent sulfur.

The contents of the reactor were stirred to 600 rpm and the temperature was ramped to 50°C and 88.4 grams of monomethylamine was added over a period of 1/2 hour. The temperature was ramped to 70°C to 95°C over the next 1 hour, cooling being employed if necessary to keep the temperature below 95°C. Next, the temperature was ramped to 140°C for 1/2 hour, and then held at 140°C for 1/2 hour. At the end of this time period, the vacuum was broken with air and 244.4 grams of 150 Neutral oil, which contained 0.278 and 0.374 percent sulfur, was added to the reactor. The reactor was cooled from 80°C to 90°C, and the following additional components were added to the reactor:

1 Table I below lists the components that were varied in Examples 1-29.

2

3

Table I

4

Ex.	Amount of Reaction Components Charge Mole Ratio relative to the Alkylphenol						
	Diethylene- triamine	Ethanol- amine	Monomethyl- amine	1,4- Phenylene -diamine	N,phenyl- 1,4- phenylene- diamine	Ethylene Glycol	Ethylene Carbonate
1	-	-	0.987	-	-	0.328	0.394
2	-	-	0.987	-	-	0.328	0.453
3	-	-	0.914	-	-	0.298	0.358
4	-	-	0.942	-	-	0.284	0.358
5	-	-	0.970	-	-	0.284	0.358
6	-	-	0.987	-	-	0.328	0.634
7	-	-	0.987	-	-	0.328	0.634
8	1.000	-	-	-	-	0.328	0.394
9	1.000	-	-	-	-	0.328	1.000
10	1.000	-	-	-	-	0.328	0.697
11	1.000	-	-	-	-	0.328	1.000
12	0.667	-	-	-	-	0.328	0.667
13	0.495	-	-	-	-	0.328	1.304
14	-	0.997	-	0.499	-	0.328	0.394
15	-	0.997	-	-	-	0.284	0.358
16	-	1.047	-	-	-	0.284	0.358
17	-	1.047	-	-	-	0.284	0.358
18	-	1.047	-	-	-	0.284	0.376
19	-	1.047	-	-	-	0.284	0.376
20	-	1.047	-	-	-	0.284	0.376
21	-	1.152	-	-	-	0.284	0.376
22	-	1.204	-	-	-	0.284	0.376
23	-	1.256	-	-	-	0.284	0.376
24	-	1.047	-	-	-	0.284	0.376
25	-	1.047	-	-	-	0.284	0.395
26	-	1.047	-	-	-	0.284	0.413
27	-	1.047	-	-	-	0.284	0.434
28	-	1.047	-	-	-	0.284	0.456
29	-	-	-	-	1.000	0.284	0.413

5

6

7 The results obtained for Examples 1-29 are given below in Tables II to V.

8

1 Table II shows the results obtained when monomethyl amine was used to
2 make the Mannich bases.

3 Table II
4

Ex.	CO ₂ /Ca	TBN	Sulfur (weight %)	Viscosity (cSt at 100°C)	Sediment (volume %)
1	0.394	159	0.21	154	NA *
2	0.425	188	0.17	219	12.0
3	0.424	200	0.20	402	3.6
4	0.350	196	0.16	551	4.8
5	0.342	207	0.17	693	1.4
6	0.422	186	0.20	103	4.0
7	0.492	180	0.14	214	10.0

5
6 * Data are not available.

7 Table III shows the results obtained when diethylenetriamine was used to
8 make the Mannich bases.

9
10 Table III
11

Ex.	CO ₂ /Ca	TBN	Sulfur (weight %)	Viscosity (cSt at 100°C)	Sediment (volume %)
8	0.316	258	0.18	302	11.0
9	NA *	252	0.20	609	14.0
10	0.310	221	0.16	1181	14.0
11	0.336	200	0.19	599	1.3
12	0.489	155	0.16	251	16.0

12
13 * Data are not available.

14 Table IV shows the results obtained when ethanol amine was used to make
15 the Mannich bases. No data were obtained for Example 13 because the
16 product was too solid.

17

Table IV

Ex.	CO ₂ /Ca	TBN	Sulfur (weight %)	Viscosity (cSt at 100°C)	Sediment (volume %)
14	0.436	208	0.64	852	0.8
15	0.347	216	0.16	1103	1.5
16	0.390	214	0.17	1374	0.8
17	0.385	211	0.15	1282	2.2
18	0.374	208	0.13	748	0.5
19	0.401	209	<0.05	721	0.5
20	0.392	199	0.13	685	1.2
21	0.384	209	0.15	831	0.3
22	0.400	207	<0.12	1042	0.3
23	0.385	205	<0.04	917	0.3
24	0.382	195	0.19	331	0.8
25	0.390	200	0.19	525	0.9
26	0.413	196	0.13	403	4.0
27	0.369	197	0.16	349	6.8
28	0.369	197	0.16	349	6.8

Table V shows the results obtained when N-phenyl,1,4-phenylene diamine was used to make the Mannich bases.

Table V

Ex.	CO ₂ /Ca	TBN	Sulfur (weight %)	Viscosity (cSt at 100°C)	Sediment (volume %)
29	0.144	87	0.10	374	8.0

Table VI below lists the components that were varied in Examples 30-46.

50 grams of alkylbenzene sulfonate, wherein the alkyl group on the benzene is 80 percent straight-chain C₂₀-C₂₄ and 20 percent branched-chain C₁₀-C₁₅, was added to the reaction mixture in Examples 35, 36, 38, 39 and 45.

Ethylene glycol was not added to Example 45.

Table VI

Ex.	Amount of Reaction Components Charge Mole Ratio relative to the Alkylphenol						
	Diethylene- triamine	Ethanol- amine	Monomethyl- amine	1,4- Phenylene- diamine	N,phenyl- 1,4- phenylene- diamine	Ethylene Glycol	Ethylene Carbonate
30	-	-	0.969	0.030	-	0.328	0.394
31	-	-	0.938	0.050	-	0.328	0.473
32	-	-	0.969	0.030	-	0.328	0.315
33	-	-	0.969	0.030	-	0.328	0.473
34	-	-	0.969	0.030	-	0.328	0.474
35	-	-	1.001	0.030	-	0.328	0.474
36	-	-	1.001	0.030	-	0.298	0.358
37	-	-	0.882	0.027	-	0.298	0.358
38	-	-	0.914	0.027	-	0.298	0.358
39	-	-	0.914	0.027	-	0.298	0.358
40	-	0.915	-	0.027	-	0.298	0.376
41	-	0.915	-	0.027	-	0.298	0.376
42	-	0.961	-	0.027	-	0.284	0.358
43	-	0.915	-	0.026	-	0.284	0.358
44	-	0.870	-	0.023	-	0.258	0.358
45	-	1.001	-	0.030	-	0.000	0.358
46	-	0.915	-	0.027	-	0.284	0.358

The results obtained in the above Examples 30-46 in Table VI are given below in Tables VII and VIII.

Table VII shows the results obtained when a combination of two amines, monomethyl amine and 1,4-phenylene diamine, was used to make the Mannich bases.

Table VII

Ex.	CO ₂ /Ca	TBN	Sulfur (weight %)	Viscosity (cSt at 100°C)	Sediment (volume %)
30	0.413	194	0.19	307	5.6
31	0.425	176	0.17	175	6.0
32	0.411	186	NA *	284	8.4
33	NA *	152	0.23	117	9.2

34	0.397	154	0.19	100	NA *
35	0.446	160	0.23	89	12.3
36	0.414	171	0.27	113	NA *
37	0.455	197	0.23	502	3.2
38	0.450	193	0.26	NA *	3.2
39	0.454	190	<0.06	178	5.0

1

2 * Data are not available.

3 Table VIII shows the results obtained when a combination of two amines,
4 ethanol amine and 1,4-phenylene diamine, was used to make the Mannich
5 bases.

6

7

8

Table VIII

Ex.	CO ₂ /Ca	TBN	Sulfur (weight %)	Viscosity (cSt at 100°C)	Sediment (volume %)
40	0.437	183	0.25	573	NA *
41	0.356	190	0.08	681	5.6
42	0.347	196	0.07	947	2.4
43	0.323	203	0.05	926	2.4
44	0.349	195	0.19	967	2.2
44	0.386	195	0.0	966	4.0
45	0.385	102	0.21	59	10.4
46	0.350	201	0.00	589	4.0

9

10 * Data are not available.

11

Examples A-E

12 The preparation of carbonated, overbased Mannich condensation
13 products of alkylphenols using ethylene glycol and carbon dioxide

14

15 Examples A-E experiments were conducted using the same procedure as
16 used for Examples 30-46 above, except the ethylene carbonate was replaced
17 with ethylene glycol and carbon dioxide for the carbonation of Mannich
18 condensation products of alkylphenols. Components kept constant in
19 Examples A-E were the Charge Mole Ratio of paraformaldehyde at 1.942, of

1 Ca(OH)₂ at 0.899, and of water at 0.362. Ethylene glycol was added over a
2 period of 1/2 hour and the carbon dioxide was added over a period of 1 hour.

3

4 In Examples A-D, 50 grams of alkylbenzene sulfonate, wherein the alkyl
5 group on the benzene is 80 percent straight-chain C₂₀-C₂₄ and 20 percent
6 branched-chain C₁₀-C₁₅ was added to the reaction mixture.

7

8 Table A below shows the components used in Examples A-E.

9

10

Table A

11

Ex.	Amount of Reaction Components Charge Mole Ratio relative to the Alkylphenol						
	Diethylene- triamine	Ethanol- amine	Monomethyl- amine	1,4- Phenylene- diamine	N-phenyl- 1,4- phenylene -diamine	Ethylene Glycol	CO ₂
A	-	-	-	0.027	-	0.238	0.655
B	-	-	1.001	0.060	-	0.238	0.818
C	-	-	0.969	0.030	-	0.328	0.788
D	-	-	0.969	0.030	-	0.328	0.788
E	-	-	0.882	0.027	-	0.656	0.358

12

13 The results obtained for Examples A-E are given below in Table B.

14

15

Table B

Ex.	CO ₂ /Ca	TBN	Sulfur (weight %)	Viscosity (cSt at 100°C)	Sediment (volume %)
A	0.480	134	0.29	78	NA *
B	0.600	130	0.17	88	NA *
C	0.375	140	0.29	162	8.0
D	0.564	149	0.26	235	7.2
E	0.456	198	0.31	434	7.2

16

17 * Data are not available.